

# NEW PROCESSING METHODS FOR PRODUCING LEAD AND ELEMENTAL SULFUR FROM ORES

B. Golomeov, B. Krstev, M. Golomeova

University "Goce Delcev" Stip, Faculty of Natural & Technical Sciences - Stip, Macedonia

A. Krstev

University "Goce Delcev" Stip, Faculty of Computer Science, Stip, Macedonia

## ABSTRACT

*These investigations have developed an effective hydrometallurgical method to recover high-purity lead metal and elemental sulfur from simulated galena synthetic mixtures eliminating sulfur gases and lead emissions, in contrast to the current high-temperature smelting technology.*

*The method consists of different operations: oxidative leaching with production of solution with residue containing elemental sulfur., electrowinning by the solution with metal production.*

*The obtained results determined the optimal parameters for possible processing of natural domestic galena ores.*

**Keywords:** leaching, lead, sulfur, synthetic mixtures

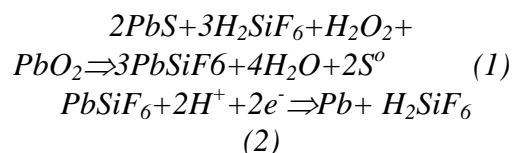
## 1. INTRODUCTION

A major cost factor in the sintering and smelting process for producing Pb is the control needed to meet existing environmental standards for Pb emissions. Another issue is the current concern over acid rain, which will in all probability result in even more stringent controls on emission of sulfur gases.

Processing of the galena mixtures or concentrates is developed as an effective low-temperature leaching-electrowinning method to produce Pb metal and elemental sulfur from galena mixtures or concentrates. The method reduces Pb emissions and totally eliminates the formation of sulfur gases. The elemental S produced is more economical to store and ship than the sulfuric acid ( $H_2SO_4$ ) generated by the high-temperature smelting process.

This hydrometallurgical method consists of leaching galena synthetic mixtures or

concentrates in waste fluosilicic acid ( $H_2SiF_6$ ) with hydrogen peroxide ( $H_2O_2$ ) and lead dioxide ( $PbO_2$ ) as oxidants at  $95^\circ$ , electrowinning the ( $PbSiF_6$ ) solution at  $35^\circ$  to produce 99,99% Pb metal, and solvent extraction to recover S, leaving a residue containing eventually present Cu, Ag, and other metal values.



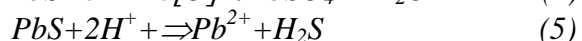
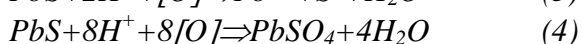
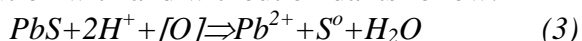
Several galena leaching processes have been investigated, including processing using ferric chloride, ferric sulfate, nitric acid and ammonium acetate solutions. The leached  $PbCl_2$  and  $PbSO_4$  salts have a very limited solubility in aqueous solution, making aqueous electrolysis difficult. Lead metal was recoverable from  $PbCl_2$

by molten-salt electrolysis operated at 450°. It's known that electrowinning of Pb in  $HNO_3$  and  $H_2SiF_6$  solutions yields Pb metal at the cathodes and at the same time  $PbO_2$  at the anodes.

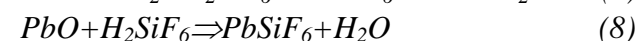
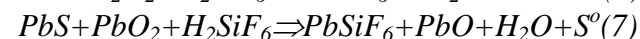
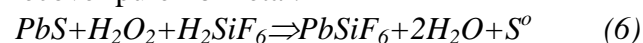
The next text will explain the oxidative leaching-electrowinning process. The parameters for leaching process about synthetic mixtures were investigated in laboratory experiments.

## 2. GENERAL

The chemical equations for PbS leaching in acid solution with and without oxidants follow:



Reaction (3) shows that oxidative leaching of PbS will yield Pb salt and elemental S. Reaction (4) suggests  $PbSO_4$  may form if the redox potential of the solution is too high, and reaction (5) indicates  $H_2S$  will form when leaching in acid solution if the redox potential is too low. To avoid the generation of  $H_2S$  one-fourth of the required oxidant have to be added to the  $H_2SiF_6$  solution prior to the addition to the PbS. The reaction is exothermic and it's necessary to add  $H_2O_2$  slowly through a burette to avoid overheating the leach solution. After adding the  $H_2O_2$ ,  $PbO_2$  was added slowly to control the redox potential. The reactions occurring during the oxidative leaching of PbS synthetic mixtures or concentrates with  $H_2SiF_6$  are shown below. At the end of leaching, the mixture was filtered to separate the leachate from the residue. The residue consisted of elemental S and other metal values. The leachate is sent to electrowinning to recover pure Pb metal.



### 2.1 Previous investigations

As leaching parameters were investigated: PbS samples of 98% on the -400 mesh or 96% on the as-received concentrates if  $H_2O_2$  and  $PbO_2$  were used as oxidants (the possible oxidants may be air, oxygen, ozone,  $HNO_3$  and  $MnO_2$ ); leaching temperature from 50-95°; leaching time from 35-335 min. The results of carried out investigations follow:

**Table 1.** Effect of various amounts of oxidants

| Test | $H_2O_2$ 35%-ml | $PbO_2$ gr. | Pb%  |
|------|-----------------|-------------|------|
| 1    | 0,0             | 16,0        | 92,0 |
| 2    | 2,5             | 17,0        | 95,0 |
| 3    | 5,0             | 9,8         | 95,0 |
| 4    | 7,5             | 8,1         | 96,8 |
| 5    | 10,0            | 5,7         | 95,1 |
| 6    | 19,0            | 0,0         | 96,0 |

**Table 2.** Effect of time and temperature

| Leach temperature<br>T°C | Leach time,<br>(min) | Pb%  |
|--------------------------|----------------------|------|
| 50                       | 335                  | 62,3 |
| 70                       | 240                  | 91,5 |
| 80                       | 90                   | 76,0 |
| 90                       | 75                   | 90,1 |
| 90                       | 90                   | 97,5 |
| 95                       | 35                   | 96,0 |
| 95                       | 75                   | 96,5 |

**Table 3.** Effect of leach time in Pb extraction

|                 | Leach time |         |         |
|-----------------|------------|---------|---------|
|                 | 30 min     | 60 min  | 90 min  |
| Pb%             | 92,3       | 95,6    | 96,4    |
| Leachate, g/l:  |            |         |         |
| Pb.....         | 163,500    | 176,700 | 180,300 |
| $H_2SiF_6$ .... | 62,900     | 55,400  | 52,300  |
| Zn.....         | 0,540      | 0,619   | 0,683   |
| Fe.....         | 0,369      | 0,415   | 0,091   |
| Cu.....         | 0,050      | 0,091   | 0,109   |
| Co.....         | 0,006      | 0,007   | 0,007   |
| Ni.....         | 0,012      | 0,014   | 0,007   |

**Table 4.** Effect of  $H_2SiF_6$  concentration

|                 | $H_2SiF_6$ -technical-grade acid |         |         |         |
|-----------------|----------------------------------|---------|---------|---------|
|                 | 175 g/l                          | 200 g/l | 250 g/l | 300 g/l |
| Pb%             | 89,0                             | 97,5    | 95,4    | 95,7    |
| Leachate, g/l   |                                  |         |         |         |
| :               | 180                              | 179     | 184     | 177     |
| Pb.....         | 32                               | 56      | 94      | 133     |
| $H_2SiF_6$ .... | 0,57                             | 0,75    | 0,82    | 1,00    |
| Zn.....         | 0,53                             | 0,61    | 0,61    | 0,67    |
| Fe.....         | 0,12                             | 0,13    | 0,13    | 0,18    |
| Cu.....         | 0,00                             | 0,00    | 0,00    | 0,00    |
| Co.....         | 0,02                             | 0,02    | 0,02    | 0,02    |
| Ni.....         |                                  |         |         |         |

The effect of using different combinations of oxidants of  $H_2O_2$  and  $PbO_2$  on PbS leaching was

insignificant. Previous leaching experiments showed that  $H_2O_2$  was a more efficient oxidizer to initiate the leach reaction. Also, it was less expensive than  $PbO_2$ . Thus, it is beneficial to use  $H_2O_2$  to leach PbS and only use  $PbO_2$  at the end of the leach to void oxidizing PbS into  $PbSO_4$ .

Leaching temperatures had a great influence on reaction rate and Pb extraction. When leaching below  $80^\circ C$ , the reaction rate was thought to be too slow for any practical application. Lead extraction was 96% when leaching at  $95^\circ C$  for 35 min using  $H_2O_2$  and  $PbO_2$  as oxidants. The leaching rate increased greatly and the required leaching time was reduced from 90 min to 35 min as the temperature increased from  $90^\circ C$  to  $95^\circ C$ . Lead extraction was increased from 92% to 96% as leaching time increased from 30 min to 60 min at  $95^\circ C$ . Initial leaching was rapid, but the elemental sulfur formed and coated the PbS particles, further reaction was probably diffusion controlled and the leach rate was reduced. However, the effect of the sulfur coating was not critical, because of the fine particle size of the PbS.

The amounts of PbS,  $PbO_2$  and  $H_2SiF_6$  used in a leach test determined the concentration of  $PbSiF_6$  and free  $H_2SiF_6$  in the pregnant leachate. Increasing the concentration of free  $H_2SiF_6$  above 60 g/lit had no significant effect on the Pb extraction, extraction of impurities decreased with decreasing concentration of free  $H_2SiF_6$ . Lead extraction of 96%, 91% and 96% were achieved using  $H_2SiF_6$  solutions made from technical-grade, waste, and recycled acid. Waste  $H_2SiF_6$  contained HCl and  $H_2SO_4$  as impurities, which formed some insoluble Pb salts during leaching, resulting in lower Pb extraction. Recycled electrolyte, in which impurities were removed during prior leaching, was as reactive as technical-grade  $H_2SiF_6$ .

### 3. EXPERIMENTAL TESTS

The conditions by the leaching process of the synthetic galena mixtures (PbS) with gangue mineral's compounds (ZnS, CuS, NiS, CoS, CaO, MgO,  $Fe_2O_3$ ,  $SiO_2$ ) and oxidants addition  $H_2O_2$  and  $PbO_2$ , leaching temperature ( $^\circ C$ ) with retaining leaching time (min) in the presence of technical  $H_2SiF_6$  is shown on the following tables.

**Table 5.** Chemistry composition of the synthetic mixtures

| Compounds | Synthetic mixtures (%) |         |         |
|-----------|------------------------|---------|---------|
|           | I                      | II      | III     |
| Pb        | 50.000                 | 60.000  |         |
| PbS       | 57.740                 | 70.000  | 80.830  |
| ZnS       | 5.000                  | 5.000   | 5.000   |
| CuS       | 1.000                  | 1.000   | 1.000   |
|           | 0.050                  | 0.050   | 0.050   |
| $Fe_2O_3$ | 1.010                  | 1.050   | 1.020   |
| $SiO_2$   | 29.200                 | 16.900  | 6.100   |
| $Al_2O_3$ | 2.000                  | 2.000   | 2.000   |
| CaO       | 2.000                  | 2.000   | 2.000   |
| MgO       | 2.000                  | 2.000   | 2.000   |
| Total     | 100.000                | 100.000 | 100.000 |

**Table 6.** Effect of various amounts of oxidants

| Test<br>(Pb-70%) | $H_2O_2$ -<br>35%<br>ml | $PbO_2$ ,<br>gr | Pb<br>(%) |
|------------------|-------------------------|-----------------|-----------|
| 1                | 0,0                     | 15,0            | 90,0      |
| 2                | 2,5                     | 15,0            | 95,0      |
| 3                | 5,0                     | 9,5             | 95,0      |
| 4                | 7,5                     | 8,0             | 96,5      |
| 5                | 10,0                    | 5,0             | 95,0      |
| 6                | 19,0                    | 0               | 96,0      |

**Table 7.** 35%  $H_2O_2$  (7,5 ml);  $PbO_2$  (8 gr)

|                               | $H_2SiF_6$  |             |             |             |
|-------------------------------|-------------|-------------|-------------|-------------|
|                               | 175<br>gr/l | 200<br>gr/l | 250<br>gr/l | 300<br>gr/l |
| Pb(%)                         | 85,0        | 97,5        | 95,0        | 95,5        |
| Analysis of<br>leachate, gr/l |             |             |             |             |
| Pb.....                       | 180         | 175         | 185         | 175         |
| $H_2SiF_6$ .....              | 30          | 55          | 90          | 130         |
| Zn.....                       | 0,55        | 0,75        | 0,80        | 1,00        |
| Fe.....                       | 0,50        | 0,60        | 0,60        | 0,65        |
| Ni.....                       | 0,10        | 0,10        | 0,10        | 0,2         |
| Cu.....                       | 0,015       | 0,02        | 0,02        | 0,02        |

**Table 8.** 35%  $H_2O_2$  (7,5 ml);  $PbO_2$  (8 gr);  $H_2SiF_6$  (200 gr/l)

| $Pb\%$ | $T^{\circ}C$ | $t(min)$ | $Pb\%$ |
|--------|--------------|----------|--------|
| 50%    | 70           | 30       | 52,5   |
|        |              | 60       | 56,5   |
|        |              | 90       | 65,3   |
|        | 80           | 30       | 54,2   |
|        |              | 60       | 58,5   |
|        |              | 90       | 67,0   |
|        |              | 30       | 56,5   |
|        |              | 60       | 59,1   |
|        |              | 90       | 70,0   |
|        | 90           | 30       | 55,6   |
|        |              | 60       | 60,2   |
|        |              | 90       | 68,7   |
| 60%    | 70           | 30       | 57,2   |
|        |              | 60       | 63,3   |
|        |              | 90       | 71,5   |
|        | 80           | 30       | 57,0   |
|        |              | 60       | 61,0   |
|        |              | 90       | 73,5   |
|        | 90           | 30       | 60,5   |
|        |              | 60       | 63,8   |
|        |              | 90       | 75,0   |
| 70%    | 70           | 30       | 65,0   |
|        |              | 60       | 72,0   |
|        |              | 90       | 79,0   |
|        | 80           | 30       | 87,6   |
|        |              | 60       | 95,3   |
|        |              | 90       | 97,6   |
|        | 90           | 30       |        |
|        |              | 60       |        |
|        |              | 90       |        |

#### 4. CONCLUSIONS

Above mentioned combined hydrometallurgical and electrometallurgical methods are developed to produce lead and elemental S from synthetic mixtures or concentrates with high purity. Contemporary, this process eliminates S gases and Pb emissions. The elemental S produced is easier to transport and store than is the  $H_2SO_4$  generated by the pyrometallurgical methods.

Investigated experiments and tests included oxidative leaching of PbS in synthetic mixtures with  $H_2SiF_6$ , electrowinning the leach solution to produce high-purity lead metal, carbon treatment of spent electrolyte for recycling, and S removal from the leach residue. Investigated experiments by PbS synthetic mixtures show satisfactory Pb extraction and

appropriate possibility for treatment of natural ore samples and concentrates produced in industrial mineral processing lead-zinc plants in the Republic of Macedonia.

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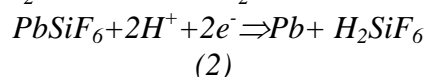
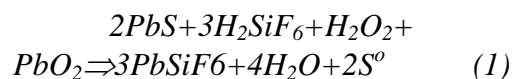
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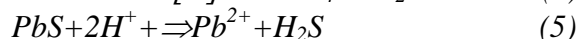
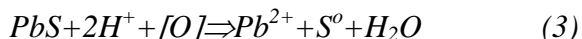
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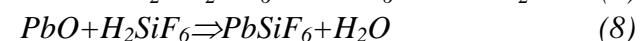
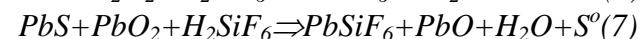
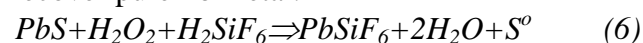
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**Table 2.** Effect of time and temperature

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| 70                       | 240                  | 91,5 |
| 80                       | 90                   | 76,0 |
| 90                       | 75                   | 90,1 |
| 90                       | 90                   | 97,5 |
| 95                       | 35                   | 96,0 |
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**Table 3.** Effect of leach time in Pb extraction

|                 | Leach time |         |         |
|-----------------|------------|---------|---------|
|                 | 30 min     | 60 min  | 90 min  |
| Pb%             | 92,3       | 95,6    | 96,4    |
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| Leachate, g/l   |                                  |         |         |         |
| :               | 180                              | 179     | 184     | 177     |
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| $H_2SiF_6$ .... | 0,57                             | 0,75    | 0,82    | 1,00    |
| Zn.....         | 0,53                             | 0,61    | 0,61    | 0,67    |
| Fe.....         | 0,12                             | 0,13    | 0,13    | 0,18    |
| Cu.....         | 0,00                             | 0,00    | 0,00    | 0,00    |
| Co.....         | 0,02                             | 0,02    | 0,02    | 0,02    |
| Ni.....         |                                  |         |         |         |

The effect of using different combinations of oxidants of  $H_2O_2$  and  $PbO_2$  on PbS leaching was

insignificant. Previous leaching experiments showed that  $H_2O_2$  was a more efficient oxidizer to initiate the leach reaction. Also, it was less expensive than  $PbO_2$ . Thus, it is beneficial to use  $H_2O_2$  to leach PbS and only use  $PbO_2$  at the end of the leach to void oxidizing PbS into  $PbSO_4$ .

Leaching temperatures had a great influence on reaction rate and Pb extraction. When leaching below  $80^\circ C$ , the reaction rate was thought to be too slow for any practical application. Lead extraction was 96% when leaching at  $95^\circ C$  for 35 min using  $H_2O_2$  and  $PbO_2$  as oxidants. The leaching rate increased greatly and the required leaching time was reduced from 90 min to 35 min as the temperature increased from  $90^\circ C$  to  $95^\circ C$ . Lead extraction was increased from 92% to 96% as leaching time increased from 30 min to 60 min at  $95^\circ C$ . Initial leaching was rapid, but the elemental sulfur formed and coated the PbS particles, further reaction was probably diffusion controlled and the leach rate was reduced. However, the effect of the sulfur coating was not critical, because of the fine particle size of the PbS.

The amounts of PbS,  $PbO_2$  and  $H_2SiF_6$  used in a leach test determined the concentration of  $PbSiF_6$  and free  $H_2SiF_6$  in the pregnant leachate. Increasing the concentration of free  $H_2SiF_6$  above 60 g/lit had no significant effect on the Pb extraction, extraction of impurities decreased with decreasing concentration of free  $H_2SiF_6$ . Lead extraction of 96%, 91% and 96% were achieved using  $H_2SiF_6$  solutions made from technical-grade, waste, and recycled acid. Waste  $H_2SiF_6$  contained HCl and  $H_2SO_4$  as impurities, which formed some insoluble Pb salts during leaching, resulting in lower Pb extraction. Recycled electrolyte, in which impurities were removed during prior leaching, was as reactive as technical-grade  $H_2SiF_6$ .

### 3. EXPERIMENTAL TESTS

The conditions by the leaching process of the synthetic galena mixtures (PbS) with gangue mineral's compounds (ZnS, CuS, NiS, CoS, CaO, MgO,  $Fe_2O_3$ ,  $SiO_2$ ) and oxidants addition  $H_2O_2$  and  $PbO_2$ , leaching temperature ( $^\circ C$ ) with retaining leaching time (min) in the presence of technical  $H_2SiF_6$  is shown on the following tables.

**Table 5.** Chemistry composition of the synthetic mixtures

| Compounds | Synthetic mixtures (%) |         |         |
|-----------|------------------------|---------|---------|
|           | I                      | II      | III     |
| Pb        | 50.000                 | 60.000  |         |
| PbS       | 57.740                 | 70.000  | 80.830  |
| ZnS       | 5.000                  | 5.000   | 5.000   |
| CuS       | 1.000                  | 1.000   | 1.000   |
|           | 0.050                  | 0.050   | 0.050   |
| $Fe_2O_3$ | 1.010                  | 1.050   | 1.020   |
| $SiO_2$   | 29.200                 | 16.900  | 6.100   |
| $Al_2O_3$ | 2.000                  | 2.000   | 2.000   |
| CaO       | 2.000                  | 2.000   | 2.000   |
| MgO       | 2.000                  | 2.000   | 2.000   |
| Total     | 100.000                | 100.000 | 100.000 |

**Table 6.** Effect of various amounts of oxidants

| Test<br>(Pb-70%) | $H_2O_2$ -<br>35%<br>ml | $PbO_2$ ,<br>gr | Pb<br>(%) |
|------------------|-------------------------|-----------------|-----------|
| 1                | 0,0                     | 15,0            | 90,0      |
| 2                | 2,5                     | 15,0            | 95,0      |
| 3                | 5,0                     | 9,5             | 95,0      |
| 4                | 7,5                     | 8,0             | 96,5      |
| 5                | 10,0                    | 5,0             | 95,0      |
| 6                | 19,0                    | 0               | 96,0      |

**Table 7.** 35%  $H_2O_2$  (7,5 ml);  $PbO_2$  (8 gr)

|                               | $H_2SiF_6$  |             |             |             |
|-------------------------------|-------------|-------------|-------------|-------------|
|                               | 175<br>gr/l | 200<br>gr/l | 250<br>gr/l | 300<br>gr/l |
| Pb(%)                         | 85,0        | 97,5        | 95,0        | 95,5        |
| Analysis of<br>leachate, gr/l |             |             |             |             |
| Pb.....                       | 180         | 175         | 185         | 175         |
| $H_2SiF_6$ .....              | 30          | 55          | 90          | 130         |
| Zn.....                       | 0,55        | 0,75        | 0,80        | 1,00        |
| Fe.....                       | 0,50        | 0,60        | 0,60        | 0,65        |
| Ni.....                       | 0,10        | 0,10        | 0,10        | 0,2         |
| Cu.....                       | 0,015       | 0,02        | 0,02        | 0,02        |

**Table 8.** 35%  $H_2O_2$  (7,5 ml);  $PbO_2$  (8 gr);  $H_2SiF_6$  (200 gr/l)

| $Pb\%$ | $T^{\circ}C$ | $t(min)$ | $Pb\%$ |      |
|--------|--------------|----------|--------|------|
| 50%    | 70           | 30       | 52,5   |      |
|        |              | 60       | 56,5   |      |
|        |              | 90       | 65,3   |      |
|        | 80           | 30       | 54,2   |      |
|        |              | 60       | 58,5   |      |
|        |              | 90       | 67,0   |      |
|        |              | 30       | 56,5   |      |
|        |              | 90       | 60     | 59,1 |
|        |              |          | 90     | 70,0 |
|        | 60%          | 70       | 30     | 55,6 |
|        |              |          | 60     | 60,2 |
|        |              |          | 90     | 68,7 |
| 80     |              | 30       | 57,2   |      |
|        |              | 60       | 63,3   |      |
|        |              | 90       | 71,5   |      |
|        |              | 30       | 57,0   |      |
|        |              | 90       | 60     | 61,0 |
|        |              |          | 90     | 73,5 |
| 70%    |              | 70       | 30     | 60,5 |
|        |              |          | 60     | 63,8 |
|        |              |          | 90     | 75,0 |
|        | 80           | 30       | 65,0   |      |
|        |              | 60       | 72,0   |      |
|        |              | 90       | 79,0   |      |
|        |              | 30       | 87,6   |      |
|        |              | 90       | 60     | 95,3 |
|        |              |          | 90     | 97,6 |

#### 4. CONCLUSIONS

Above mentioned combined hydrometallurgical and electrometallurgical methods are developed to produce lead and elemental S from synthetic mixtures or concentrates with high purity. Contemporary, this process eliminates S gases and Pb emissions. The elemental S produced is easier to transport and store than is the  $H_2SO_4$  generated by the pyrometallurgical methods.

Investigated experiments and tests included oxidative leaching of PbS in synthetic mixtures with  $H_2SiF_6$ , electrowinning the leach solution to produce high-purity lead metal, carbon treatment of spent electrolyte for recycling, and S removal from the leach residue. Investigated experiments by PbS synthetic mixtures show satisfactory Pb extraction and

appropriate possibility for treatment of natural ore samples and concentrates produced in industrial mineral processing lead-zinc plants in the Republic of Macedonia.

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